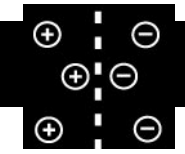
WATER TREATMENT



Overview: Ion Exchange

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Introduction

Ion exchange resins are used for many water treatment applications. Of these applications, in terms of the volume of resins used, water softening and demineralization of water are the most significant. Water softening has been practiced commercially for a century or more, making use of a wide range of natural and synthetic products. As the variety of uses for purified water has increased, so has the need to soften and demineralize water. Demineralization has only been practiced since the discovery of synthetic anion exchange resins in the 1920s. Their usefulness increased greatly with the invention of strongly basic anion exchange resins, which can remove weakly acidic compounds such as silica and carbon dioxide, as well as mineral acids. This process of ion exchange can be used as a simple method to produce water of very high purity. In general, as industrial and domestic requirements have grown, specifications for water quality have become progressively more stringent, and regulations to enforce these have become more strict. Hence the choice of resin types for a particular application becomes increasingly complex.

Applications of Ion Exchange in Water Treatment

A wide variety of new water treatment applications employ ion exchange resins in limited volume and there is limited use in niche areas for many special resin types. However, reverse osmosis (RO) is increasingly being used instead of ion exchange where treated water quality requirements are not particularly high. The use of RO followed by an ion exchange polishing process is often used for the production of high purity water, for example in the manufacture of silicon chips for the computer industry. **Table 1** lists the major water treatment processes in which ion exchange resins are used.

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Principles of Ion Exchange Applicable to Water Softening

The properties and theoretical principles of ion exchange resins are fully covered elsewhere. This article

Table 1 Major water treatment processes

Process	*Resins used*	*Significant property*	*Application areas*
Softening	SAC	Hardness selectivity	Domestic, industrial processes, food processing, etc.
Partial softening Dealkalization	WAC WAC	Temporary hardness removal and alkalinity removal	Potable water, beverage industry, industrial processes, laundry, glass washing
Demineralization	WAC, SAC WBA, SBA	Removal of cations Removal of anions	Industrial water processes Steam generation, food processing industry, process water for pharmaceutical use, etc.
Nitrate removal	SBA	Nitrate selectivity	Potable water, food and beverage processing
Metals removal	WAC chelate resins	Selectivity for heavy metals	Wastewater treatment
Sorption	Macronets WBA, SBA	Selectivity for organics	Organic scavenging

Key: WAC, weak acid cation resin; WBA, weak base anion resin; SAC, strong acid cation resin; SBA, strong base anion resin; chelate, chelating ion exchange resin; macronet, special resin with adsorption properties.

discusses only those principles that directly relate to operating performance of the ion exchange resins that are currently used in water treatment.

Ion Exchange Equilibria

Water softening is a very efficient process. Water containing hardness ions (calcium and magnesium) is passed through a cation exchange resin in the sodium form. In dilute solution, the hardness ions are selectively held:

$$K_{Na}^{Ca} = ([Ca_R]/[Na_R^2]) \times ([Na_S^2]/[Ca_S]) \times C_S/C_R \quad [1]$$

where K is a simplified selectivity coefficient describing the equilibrium. [Ca] is the calcium concentration, [Na] is the sodium concentration, and C is the overall ionic concentration. Subscripts R and S represent resin and solution phase, respectively. This equation takes no account of activity coefficients, but nevertheless can be used, certainly for comparative purposes, and usually gives fairly accurate predictions. Clearly the larger the value of K_{Na}^{Ca}, the greater the fraction of calcium residing in the resin phase. Tables of selectivity coefficients have been compiled for a wide variety of cations and anions.

Selectivity for Hardness in Softening and Resin Regeneration

The more dilute the ionic concentration, the higher the calcium (and magnesium) fraction in the resin phase, and the less calcium is needed in the solution phase to satisfy the equation. However, when considering regeneration, the ionic concentration in solution is much higher, so as C_S/C_R tends to a value greater than 1, so less calcium is needed in the resin phase to satisfy the equation. The poorer selectivity of the resin sites for calcium present in high ionic concentrations ensures that the regeneration stage is very efficient. The principle of this equation applies to all comparisons between monovalent ions such as sodium and divalent ions such as calcium. Since magnesium, the other main contributor to total hardness, is also divalent, the principles described apply equally to magnesium. In order that the regeneration process is reasonably efficient, there must be an excess of sodium ions.

Reverse Osmosis

One of the advantages of RO is that no regenerant chemicals are required. The disadvantages of RO is that capital costs are higher and pumping costs can also be high. In addition, the volume of the reject waste can be large, even though the ionic concentration within the reject is quite low. There is also a risk of membrane fouling. Generally when the total dissolved solids (TDS) in the treated water are high, RO is preferred. However, as both processes are constantly changing in efficiency, the commercial breakeven cost point is constantly changing.

Water Quality and Regeneration Efficiency

Clearly the use of smaller quantities of regenerant would make the ion exchange softening process more efficient and competitive. It has been demonstrated that the ion exchange process must be carried out in a column if the efficiency is to be optimized. For example, regenerating calcium from a resin with sodium chloride solution simply by adding the regenerant to the resin while stirring in a beaker is very inefficient. It suffers from the disadvantage that all the calcium displaced from the ion exchange resin has the opportunity to re-enter the resin and re-occupy the ion exchange sites. On the other hand, in a column operation, the displaced ion is carried away, and cannot return to the same beads at the regeneration entry point. As more fresh regenerant is added this same principle applies to the exchange process further down the column. It has been shown that, as the regenerant contact time in the column was increased to 24 h or more, the efficiency of regeneration decreased to the point where some 25–30% fewer sites were regenerated with the same quantity of regenerant. The final lower value tended asymptotically to that obtained under batch equilibrium conditions.

Counterflow and Co-flow Regeneration

A second advantage of column operation is that those beads situated at the point of entry of the regenerant will come in contact with a vast excess of pure regenerant. This ensures that almost all of the hardness ions loaded in the previous cycle are carried away from that part of the resin bed. In a stirred batch system, the ratio of regenerant ions to hardness ions would be approximately equal in every bead, depending on the quantity and concentration of regenerant used. It follows that since the water being treated is in counterflow to that of the regeneration, this allows the treated water to pass the most highly regenerated and rinsed resin at the point of exit, thus ensuring near zero leakage of hardness. Of course, the resin bed must not be disturbed for this advantage to apply. In co-flow regeneration, any regenerant at the treated water outlet has previously been in contact with the ions to be removed, hence this part of the column is least efficiently regenerated. In the following exhaustion cycle the sodium in the water at the outlet can 'back-exchange' for the hardness residual at the column outlet. This results in a significant hardness leak-

age. To optimize the operating efficiency, the use of regenerant chemical should be cut to a minimum. This has the added advantage that less excess regenerant will pollute the environment. From the above arguments, it is easy to see why counterflow regeneration is more efficient.

Diffusion in the Regeneration Stage

Returning to eqn [1], it can be shown that reduction of the regenerant quantity to a minimum can create significant disadvantages in the softening process. When the regenerant enters the column, it will inevitably suffer some dilution with the water it displaces. As has already been explained, the lower the ionic concentration in solution, the higher the selectivity for the divalent hardness ions, so any dilution will reduce the efficiency of the regeneration process. However, this dilution at the start of the regeneration process is not a significant disadvantage, because the regenerant is in contact with resin heavily loaded with hardness ions and thus some of these ions are easy to remove. However, as the regeneration proceeds, the concentration of regenerant increases and the beads are increasingly invaded by sodium chloride. This is termed 'Donnan invasion'. In fact, the first molecule of sodium chloride is not effective in achieving any regeneration of divalent hardness because only one of the two hardness bonds is released. The positive charge of the single displaced calcium ion is satisfied with the negatively charged chloride ion.

$$R\text{–}Ca^{2+}\text{–}R + Na^{+}Cl^{-} = R^{-}\text{–}Na^{+} + R^{-}\text{–}Ca^{2+}\text{–}Cl^{-} \quad [2]$$

where R is the matrix and functional group of the strong acid cation (SAC) resin.

A second molecule of sodium chloride is clearly needed to free the hardness (calcium) ion and so allow it to start the diffusion process towards the outside of the beads.

$$R\text{–}Ca^{2+}\text{–}Cl^{-} + Na^{+}Cl^{-} = R^{-}Na^{+} + Ca^{2+}Cl_2^{-} \quad [3]$$

The general direction of the regenerant is towards the centre of the beads as the diffusion of the regenerant proceeds from the solution surrounding the beads. Any hardness ion has to move against the regenerant current to leave a particular bead. Once the regenerant has completed its diffusion path to the centre of each bead, then the outward diffusion of the regenerated hardness can presumably proceed more rapidly.

As the regeneration draws to a close, the regenerant is followed by the displacement rinse. Dilution of the regenerant by the displacement water will cause selectivity reversal, thus any hardness ion still situated inside the beads, and travelling towards the outside, will promptly displace two regenerated sodium sites. If the regenerant quantity is cut to a minimum, then the release of the calcium will be slower (see eqn [2]) and the proportion of diluted regenerant to concentrated regenerant will be greater. It follows that the shorter difusion path offers a more effective regeneration resulting from improved column efficiency.

The use of beads of a narrow size range and core shell beads with a limited diffusion path offers a superior performance; this has already been seen.

Resin Kinetics

Beads of narrow size range can also present a larger surface area of exchange to the water being treated, and therefore the kinetics of exchange may be improved. Larger beads with a shell core formation also provide ease of access to each individual ion exchange site. These features can be important where high flow rates are used. Other significant factors such as resin bed depth, operating temperature, efficient distribution and collection of the water being treated are also important.

Principles of Ion Exchange Applied to Demineralization

The principles applicable to the softening process also apply to demineralization. It is useful to discuss some of these in more detail.

Resin Selectivity

Demineralization requires an ion exchange process of at least two stages. In the first essential stage, the cations in the water to be treated are replaced with hydrogen by passing the water through strong acid cation (SAC) resin in the hydrogen form. When the resin becomes exhausted to the extent that the water is not treated to the required quality, it must be regenerated with acid.

The first stage of the demineralization process may be improved to combine the use of both a SAC resin and a weak acid cation (WAC) resin. The latter is positioned upstream. This is one of the many ways in which the efficiency of this regeneration process can be varied. Returning to the properties of SAC resins, the process is unlike softening in that there are no advantages from changes in ionic concentration when regenerating sodium. The selectivity for sodium, as compared with hydrogen, may be simplified by the following equation.

$$K_H^{Na} = ([Na_R]/[H_R]) \times ([H_S]/[Na_S]) \quad [4]$$

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where H is the hydrogen ion; all other symbols as for eqn [1].

It has been reported that K_H^{Na} varies according to the cross-linking of the SAC resin.

Counterflow Regeneration

The advantages to be obtained in water quality from operation in the counterflow mode are, perhaps, even more important than for softening. The difference between the selectivity of sodium and hydrogen is very small (in fact the coefficient lies between 1 and 2). Hence any residual sodium located near the outlet of the bed is easily displaced. Low sodium leakage is clearly an essential parameter where high water purity is required. It follows that either the whole resin bed must be highly regenerated, or the resin bed has to be operated in the counterflow mode. This ensures that the treated water at the bed outlet is in contact with highly regenerated resin containing only minute traces of sodium.

Mixed Bed

The use of a mixture of SAC resins and strong base anion (SBA) resins, regenerated separately before mixing, has generally been considered the best way to achieve treated water of the highest purity. The passage of water alternately via cation and anion resins affords the more or less continuous neutralization of acids and bases produced by contact with the previous bead of opposite charge. The disadvantage is that the component resins have to be separated before regeneration. Incomplete separation will cause the offending beads to be regenerated with the wrong regenerant, resulting in a significant deterioration in treated water quality. Techniques of rinse recycle and efficient counterflow regeneration are now producing water qualities close to that of mixed bed polishing.

Effects of Sodium Leakage

One further problem occurs if the sodium leakage is high. The treated water from the cation resin outlet (decationized water) passes through the anion resin, regenerated to the hydroxide form. In general, this is a very efficient reaction, because the process is one of neutralization of acids, so the exchange reaction is essentially non-reversible, and the only by-product of the neutralization reaction is water. However, any sodium leakage from the cation resin must be accompanied by an anion to preserve electroneutrality. At the start of the cycle, when the anion resin is freshly regenerated, the anion that accompanies sodium will usually be hydroxide. This is not particularly desirable, but is easily removed by the following mixed bed resins. However, as the resin bed exhausts, the least selective anion, in exhaustion, will accompany the sodium. This anion is usually silica. Silica can cause deposits in superheaters, boilers, turbines and condensers, so accelerating corrosion. Thus it is clear that sodium leakage carries a two-fold danger.

Anion Leakage

The very high selectivity of the anions of mineral acids for ion exchange resins usually prevents high mineral anion leakage, even though regeneration to remove all of these is rarely complete. As with softening, the efficiency of regeneration is crucial if good capacity and low leakage are required. The use of narrow size range resins can shorten the diffusion path in the regeneration process.

Regeneration Efficiency

The regeneration efficiency of cation resins has already been discussed. In the demineralization process, the regeneration efficiency of anion resins is of even more importance.

- During the actual water treatment process, the removal of anions is essentially an acid–base neutralization. Hence it is driven rapidly more or less to completion. However, the regeneration stage involves the exchange of the loaded ions for the hydroxide ion. Hence this stage is a true ion exchange process where the ions being removed are in competition with the ion being fixed on the resin. It follows that the extent of regeneration is the limiting step, dictating the operating capacity of the resin. In fact, when operating SBA resins at recommended flow rates the operation capacity is normally only 5–10% below the available regenerated capacity. In other words, the chromatographic profile is extremely sharp.
- Type I SBA resins do not regenerate easily. In fact the selectivity coefficient K_{OH}^{Cl} is approximately 15–20 for gel Type I SBA resins, and even higher for equivalent macroporous types.
- Type II and acrylic SBA resins are more easily regenerated, but have the disadvantage that they remove silica less efficiently (especially the Type II); both types have poor thermal stability.
- Recently strong base resin types have been compared in their operating performance and related properties. A Type III resin has been developed that is comparable with Type II or acrylic resins in its ease of regeneration, while having thermal stability and silica removal similar to that of a Type I resin.
- Weak base anion (WBA) resins regenerate quite easily, and can be used in conjunction with SBA resins to improve overall regeneration efficiency. However,

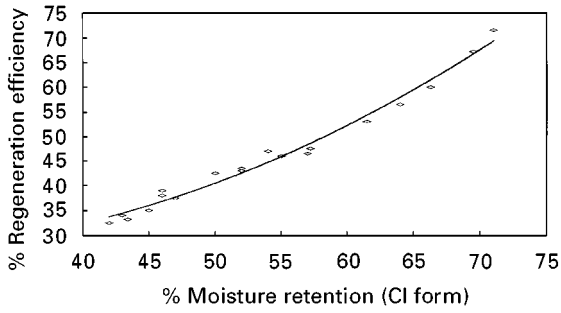

Figure 1 Regeneration efficiency of chloride form SBA Type I clear gel anion at 65 g L^{-1} NaOH.

they do not remove silica or carbon dioxide, so the proportion of WBA to SBA must be controlled to balance the needs of the process. Also the fresh regenerant must be used to regenerate the resins in the order SBA → WBA, otherwise the advantage is lost.

The mechanisms for regenerability of anion resins have been discussed in the literature. Briefly, the high selectivity for chloride, sulfate, and nitrate arises from the fact that these ions are less hydrated than is the hydroxide ion. Hence the hydroxide ion prefers to remain in the aqueous phase. As **Figure 1** shows, the lower the moisture retention of the resin, the more difficult is the regeneration process.

These mechanisms also offer good explanations for the variation in thermal stability between resin types. It has been shown that nucleophilic attack on the nitrogen of the active group by the hydroxide ion is responsible for the thermal degradation. It follows that the more hydrated the hydroxide ion, the lower the electron charge density and the lower the rate of degradation. This is confirmed by experimental data. This subject is further complicated by the differences in selectivity of chloride and sulfate ion in the regeneration process.

Principles of Dealkalization

The removal of alkalinity is a less common process than softening or demineralization, hence it will only be dealt with briefly. It has long been recognized that hardness associated with bicarbonates (termed temporary hardness) is more of a problem than that associated with mineral acids (permanent hardness). When water is heated the bicarbonate decomposes to carbon dioxide and insoluble calcium carbonate. This forms the scale that is found in the equipment used to heat or transport water. The removal of scale may be achieved by using a weak acid cation resin regenerated to the hydrogen form.

The reaction:

$$2RCOOH + CaCO_3 \rightleftarrows Ca(RCOO)_2 + CO_2 + H_2O \quad [5]$$

proceeds quite easily, while the reaction

$$RCOOH + CaCl_2 \leftrightarrows Ca(RCOO)_2 + 2HCl \quad [6]$$

does not, because the ionized acid produced inhibits further reaction.

The WAC resin is easily regenerated with a stoichiometric amount of acid. This makes the process chemically efficient but it is kinetically slow. It also has the advantage that the total dissolved solids are reduced by the removal of the hardness. The volatile carbon dioxide can be removed by deaeration. The main disadvantage is that acid is needed for regeneration.

An alternative process uses a SBA resin in the chloride form. Here the bicarbonate is exchanged for chloride directly. Thus the offending temporary hardness is exchanged for permanent hardness. There is no reduction in total dissolved solids and the operating capacity is lower, but the advantage is that the SBA resin may be regenerated with common salt.

Principles of Nitrate Removal

The World Health Organization (WHO) limit for potable water is 50 ppm of nitrate. Many water sources have higher levels, partly because of the use nitrate-based fertilizers to boost crop yields. Although this practice has been curtailed in recent years, the problem will remain for many years to come. Ion exchange resins, regenerated with sodium chloride, selectively remove nitrate in preference to bicarbonate, but not in preference to sulfate. This means that the sulfate in the water is also needlessly removed. The exchange of both nitrate and sulfate can result in the chloride level increasing above WHO limits. Where sulfate levels in the water are significant, the use of a specially developed nitrate-selective (over sulfate) resin can give increased capacity and better overall water quality.

Physical Stability of Ion Exchange Resins

Ion exchange resins have to be physically strong to last for the expected life span of 4–6 years, depending upon the resin type, temperature of operation and regeneration, ability to resist irreversible fouling from trace contaminants in the water to be treated, and adherence to the recommended operating conditions.

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This means that they have to be mechanically strong and also able to withstand rapid changes in swelling/shrinking arising from changes in ionic form and changes in ionic concentration. It is most important that the ion exchange plant is designed to accommodate the anticipated changes in bed depth, and resins should be free to adjust to the volume changes occurring naturally through the process. Tests have been developed to evaluate osmotic shock resistance; these are mentioned in other articles.

The elimination of the larger beads in the resin bed will reduce the chances of breakdown resulting from osmotic shock, because the build-up of differential stress with changes in ionic concentration is less in smaller beads. Up to now partially activated beads, which have the advantages of a smaller diffusion path described above, have not been physically stable because of the stresses developing between the swelling and shrinking of the activated part of the resin, compared with the properties of the inert core. There are indications that this difficulty is now being overcome.

Plant Design

Water analyses vary considerably, depending on the source of the water supply and the geographical area. Thus it has been impossible over the years to standardize on one type of plant or on which are the most suitable resins. **Table 2** gives on example of the water analysis information needed to design a treatment plant. Changes in total concentration of dissolved salts, the proportion of sodium and silica (as already discussed), the temperature of the water, the ratio of alkalinity to total anions, and the proportion of sulfates, chlorides and nitrates, all have an influence on the operating capacity and treated water quality.

The presence of iron can severely affect the performance of softeners. Iron can slowly accumulate and cause irreversible fouling. It also acts as a catalyst, promoting oxidation of resins that causes an increase in moisture retention and swelling of the resin. This in turn can cause stress within the resin bed, not only on the resin itself, but also on the internal collectors and distributors. The performance of demineralizers can also be affected, especially if only sulfuric acid is available for resin regeneration and resin cleaning.

Natural organic matter can vary both in quantity and quality from area to area, hence the choice of resins and preferred cycle times, the quantity of sodium hydroxide used for regeneration and its temperature as well as cleaning regimes, can vary from region to region.

Basic Principles

Developments in ion exchange resins since the 1940s have been accompanied by developments in engineering equipment and processes, from the invention of styrene-divinyl benzene resins to advances in techniques for TOC removal. The latter is now of utmost importance for the production of ultrapure water.

The basic principles of sizing an ion exchange vessel are quite simple. Let us suppose that it is necessary to treat $F\ m^3$ of water per hour, and it is required to remove C eq m^{-3}. Then the load per hour is FC mol, and FCh is the total load presented for an exhaustion cycle of h h. It is therefore possible to calculate the volume of resin needed, provided the operating capacity (O eq m^{-3}) for the particular resin is known for the specified operating conditions. If we have $V\ m^3$ of resin, then for the resin plant to treat the

Table 2 Typical water analysis information

Influent water specification	
Origin	Mains water
Pretreatments	None
Temperature	8°C
Organic matter	20.000 mg L^{-1} $KMnO_4$

Cation	*Concentration (meq L^{-1})*	*Anion*	*Concentration (meq L^{-1})*	*Other*	*Concentration (meq L^{-1})*
Ca	0.900	HCO_3	0.580	CO_2	0.010
Mg	0.140	CO_3	0.000	SiO_2	0.060
Na	0.300	Cl	0.450		
K		SO_4	0.310		
Fe		NO_3	0.000		
TC	1.340	TA	1.340		

TC, total cation concentration; TA, total anion concentration. Note that TC should equal TA. In general if there is a difference the analysis is probably incorrect. If the pH is not neutral, the hydrogen and hydroxide ions should be included in the balance.

water efficiently, the following equation must be satisfied.

$$FCh = OV$$

where h is the time in hours between successive regenerations.

Many factors can affect the operating capacity in a particular situation. This must always be lower than the total volume capacity of the resin. The most important of these factors are the regeneration level and the particular analysis of the water being treated. In certain cases other factors such as flow rate or cycle time, operating and regenerant temperature, treated water quality and cycle end point, and resin bed depth may also need to be taken into account. Furthermore, the plant itself will need to treat some extra water in order to operate successfully. This extra load needs to be allowed for in the design. The more concentrated the feed water the more extra load is placed on the resin beds. Indeed, the water may contain such a high level of dissolved salts that treatment may not be economic. In such cases RO often provides a satisfactory alternative, or as a pretreatment. When all these factors are carefully considered, the optimization of the plant becomes quite complicated, especially when taking into account the various process options and the possible choices of resin types and their various combinations. Such an exercise requires a vast experience of water treatment. To help design engineers and water treatment plant operators to make suitable design plans, computer programs are now available. In certain cases they are suitable both for new plant and to revamp or modify existing plant. They may also be used to check the current performance of a particular ion exchange line in operation, and to evaluate possible changes in operating parameters. These programs or computer printouts can be obtained from various resin manufacturers and from original engineering manufacturers to help experts in these calculations. They can also serve as useful training for those engineers learning their trade, and for water treatment chemists who need to understand the operations of a particular plant in which they have an interest.

Table 3 gives an example of data provided by a plant design computer program on the design requirements for a specified flow rate and treated water quality. **Table 4** gives an example of the engineering data provided by a computer program. Its use can save many hours in calculation time and allow exploration of the many options available before making a final choice.

Table 3 Design requirements

Operating conditions			
Flow rate per line	2.1 $m^3 h^{-1}$		
Running time	9.8 h		
Net run	21 m^3		
Treated water quality			
	Achieved	*Specified*	*End point*
Conductivity ($\mu S\ cm^{-1}$)	0.70	1.00	2.00
Silica leakage (ppb)	16	20	500
Sodium leakage (ppm)	0.038		
Residual CO_2 after SAC filter	0.59 meq L^{-1}		
Process options			
Ion exchange process	Demineralization		
Plant layout	SAC → SBA		
No. of lines	(as required)		
Resins chosen	SAC SBA		

Choice of Resins

The optimization of any given process requires considerable skill on the part of the design engineer. It is important to understand the strengths and weaknesses of each resin type so that the correct type and particle size are chosen. The design program is extremely useful to balance and match the conditions of regeneration to produce the correct quality and quantity of treated water. The combined experience of the customer and the engineer, together with the expertise and support of resin specialists, is generally regarded as the best approach to determining the optimized conditions of operation and choice of the correct equipment.

Resin Life

Provided that the design has been optimized, in all but the most difficult cases the resin life should be in the range of 4–6 years, depending on the type of resin. In fact SAC resins have been known to last very much longer, provided they are used at the optimum temperature and are kept free of contaminants and potential oxidizing agents. There must also be the provison that regenerate quantities, concentrations and flow rates are designed to avoid stress on the resins. In many cases regular checks on the state of resins can be beneficial. This will prevent build-up of chemical contaminants and highlight any maloperation before real damage is done.

See Colour Plates 125, 126.

See also: **I/Ion Exchange.**

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Table 4 Calculation of full plant design details for an ion exchange plant

		Filter	
		SAC	*SBA*
Ion exchange load			
Gross run	(m^3)	21	21
Ionic load	(eq)	28	30
Resin data			
Resin type		SAC	SBA
Resin grade		–	–
Theoretical capacity	(eq L^{-1} R)	1.15	0.62
Operational capacity	(eq L^{-1} R)	0.48	0.56
Resin volume	(L)	58	53
Flow rate	(BV h^{-1})	36.9	40.2
Organic load	(g L^{-1} $KMnO_4$)		7.880
Regeneration data			
Regeneration mode		CTF : FB	CTF : FB
Regenerant		HCl	NaOH
Concentration	%	5.0	4.0
% of Theory		345	180
Level	(g L^{-1} R)	61.0	40.0
Total	(kg 100%)	4	2
Excess	(eq)	69	24
Temperature	(°C)		25
Dilution water	(m^3)	0.1	0.0
Slow rinse	(m^3)	0.1	0.2
Fast rinse	(m^3)	Recycling	Recycling
Plant size data			
Bed depth (changing from supplied form as shown)			
Supplied form	(mm)	586	538
Exhausted form	(mm)	562	
Regenerated form	(mm)	609	634
Vessel diameter	(mm)	365	365
Cross-section	(m^2)	0.10	0.10
Cylindrical height	(mm)	Per design	Per design
Hydraulic data			
Linear velocity	(m h^{-1})	21.2	21.2
Pressure drop	(kPa)	19.0	14.8
Design factor (Limitations caused by flow rate)		0.42	0.90

Note: BV, bed volume; R, resin.

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Anion Exchangers: Ion Exchange

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Introduction

Anion exchange resins consist of a polymeric matrix to which different functional groups are attached. Most weakly basic anion exchangers contain tertiary amino groups; in a few cases primary and secondary groups are also encountered. In many cases weakly basic anion exchangers are not monofunctional but possess a variety of amino groups. Strongly basic resins contain quaternary ammonium groups. Standard commercially available exchangers contain either $-N^+(CH_3)_3$ groups (type 1 resins) or $-N^+(CH_3)_2C_2H_4OH$ groups (type 2 resins). Both weakly and strongly basic exchange resins are available in gel-type or macroporous modifications.

Properties and fields of application mainly depend on the dissociation properties of the functional groups in which dissociation plays the most important role. By means of the mass action law, dissociation constants of the protonated amino and ammonium groups can be estimated. The respective numerical values are in the range of $pK_a > 13$ for strongly basic resins and 5–8 for weakly basic resins. Therefore, strongly basic resins are protonated over the entire pH range but weakly basic exchangers are protonated at pH values below 5–8, depending on the type. As a consequence, strongly basic resins will exchange anions in both acid and alkaline solutions. In addition, these exchangers can adsorb weak acids and even ionize very weakly dissociated acids. Weakly basic resins, however, can operate only in acidic media and are unable to convert neutral salts to the respective hydroxides (e.g. NaCl to NaOH). Furthermore, they cannot normally adsorb weak acids.

The uptake of anions by resins is subject to specific interactions between counterions and co-ions and the distribution of exchangeable ions depends on the properties of both the exchanger and the ions. Consequently, a favoured sorption of certain types of anions occurs. The sequence of affinities is given either qualitatively by the selectivity series or quantitatively by, for example, separation factors. For weakly basic anion exchangers the sequence of most common anions in fresh water is:

$$OH^- \gg SO_4^{2-} > NO_3^- > Cl^-$$

Due to the dissociation properties of the functional groups, hydroxyl ions are strongly preferred. This is important for the conversion of these resins to the hydroxyl (or free base) form in the regeneration step, in which only slightly more than the stoichiometric amount of OH– bearing solutions is required.

For strongly basic anion exchangers the selectivity series is:

$$SO_4^{2-} > NO_3^- > Cl^- > HCO_3^- > OH^-$$

For these resins hydroxyl ions are the least preferred among the standard anions. Conversion of the resins to the hydroxyl form therefore requires comparatively large excess amounts of sodium hydroxide.

For elimination of nitrate anions from drinking water the preferred sorption of sulfate ions causes considerable disadvantages. Extensive research during the 1980s has shown that this drawback can be overcome by introducing functional groups which are more hydrophobic and bulkier. By these means, the ability to adsorb sulfate ions is considerably decreased. The so-called nitrate-selective resins which are now commercially available contain triethyl instead of trimethyl groups and, therefore, exhibit a reversed preference for nitrate and sulfate ions.

The rate of exchange depends mainly on the internal interdiffusion of exchanging ions. On the completely ionized strong base resins this diffusion is rather quick and the overall rate of exchange mainly depends on the particle size distribution. With weakly basic exchangers, however, the poor dissociation and further specific interactions between functional sites and diffusing ions considerably slow the rate of exchange. For these resins, both the uptake of acids and conversion to the free base form by means of sodium hydroxide strongly depend on the concentration of the liquid phases.

Strongly basic anion exchangers in the hydroxyl form are subject to considerable degradation of

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